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(10) A. N. / Gent *■* P. / Dreyfuss

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Akron, Ohio 44325

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Progress in three different phases of our study of the role of chemical bonding in adhesion is summarized in this report. Phase one consisted of an experimental study of the self- adhesion of thin layers of three crosslinked elastomers; namely, <u>cis</u> -polyisoprene (natural rubber) and two polybutadienes. For the polybutadienes, the strength of self-adhesion was found to be strongly dependent upon the time of exposure of the two		

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### Summary

Progress in three different phases of our study of the role of chemical bonding in adhesion is summarized in this report. Phase one consisted of an experimental study of the self-adhesion of thin layers of three crosslinked elastomers; namely, cis-polyisoprene (natural rubber) and two polybutadienes. For the polybutadienes, the strength of self-adhesion was found to be strongly dependent upon the time of exposure of the two surfaces to air before they were brought into contact. The same phenomenon did not take place on exposure to nitrogen nor for samples of cis-polyisoprene and it was reduced or delayed in samples containing antioxidant. It was therefore attributed to surface oxidation reactions that can lead to interfacial covalent bonds with polybutadiene but not with polyisoprene. Phase two consisted of a study of the effect of the number of chemical bonds at an interface between glass and polybutadiene on the joint strength of the adhesive bond formed between them. The radioactivity present in  $^{14}\text{C}$  labelled interfacial bonds was used as a measure of the number of chemical bonds. Joint strength was determined by the  $180^\circ$  peel test. The strength of the joint was shown to increase as the number of chemical bonds increased. Phase three consisted of a study of the effect of various levels of adhesion

between elastomer and glass bead filler on the tear strength and tensile strength of polybutadiene, which served as the model elastomer. Preliminary results indicate that good adhesion increased the nominal tensile breaking stress, but the elongation at break as well as the strain energy density at break was lower for all the filled materials. Tear strength of the filled materials was significantly greater than that of the unfilled elastomer. Calculations of the size of a Griffith crack based on the small number of samples studied so far indicate that it is generally of the same order of magnitude as the diameter of the largest glass particles present. This aspect of the study is continuing.

## Introduction

The objectives of this study have been first to obtain direct evidence for chemical bonding at the interface between similar and dissimilar materials and second to learn how the density of chemical bonds affects the work of detachment of the materials joined together. Two substantial technical reports describing some of this year's progress have recently been published. They are: Technical Report No. 5, "Bonding Elastomer Layers Together by a Surface Oxidation Reaction", by R. J. Chang, A. N. Gent, C. C. Hsu and K. C. Sehgal, October, 1979, and Technical Report No. 6, "Effect of Number of Chemical Bonds on the Strength of Adhesion Between Glass and Polybutadiene", by P. Dreyfuss, Y. Eckstein, Q.-S. Lien and H. H. Dollwet, December, 1979. Only the salient features of these studies will be included in this report.

## Results and Discussion

### 1. Effect of Surface Exposure Prior to Bonding

In the course of studies of the work of detachment of peel test specimens with polybutadiene as both the overlayer and the substrate, we observed that the strength of self-adhesion varied

not only with the degree of crosslinking between the layers as reported last year but also with the time of exposure of the two surfaces to air before they were brought into contact. The latter observation led to an experimental study of the self-adhesion of thin layers of three crosslinked elastomers: cis-polyisoprene (natural rubber) and two polybutadienes having different cis-1,4, trans-1,4 and 1,2 contents.

For some polybutadiene materials, as shown in Figures 1 and 2, the strength of self-adhesion was strongly dependent upon the time of exposure of the two surfaces to air before they were brought into contact. The strength rose so dramatically during the first hour or so of exposure that sometimes the layers could not later be forcibly separated. When the surfaces were exposed to air for longer periods before joining them, the strength of self-adhesion fell to low levels again. This remarkable enhancement in self-adhesion did not take place on exposure to nitrogen and it was reduced or delayed in samples containing added antioxidant.

Samples of polybutadiene, obtained at different times, were found to respond quite differently to air exposure. It is thought that the antioxidants added to the material by the



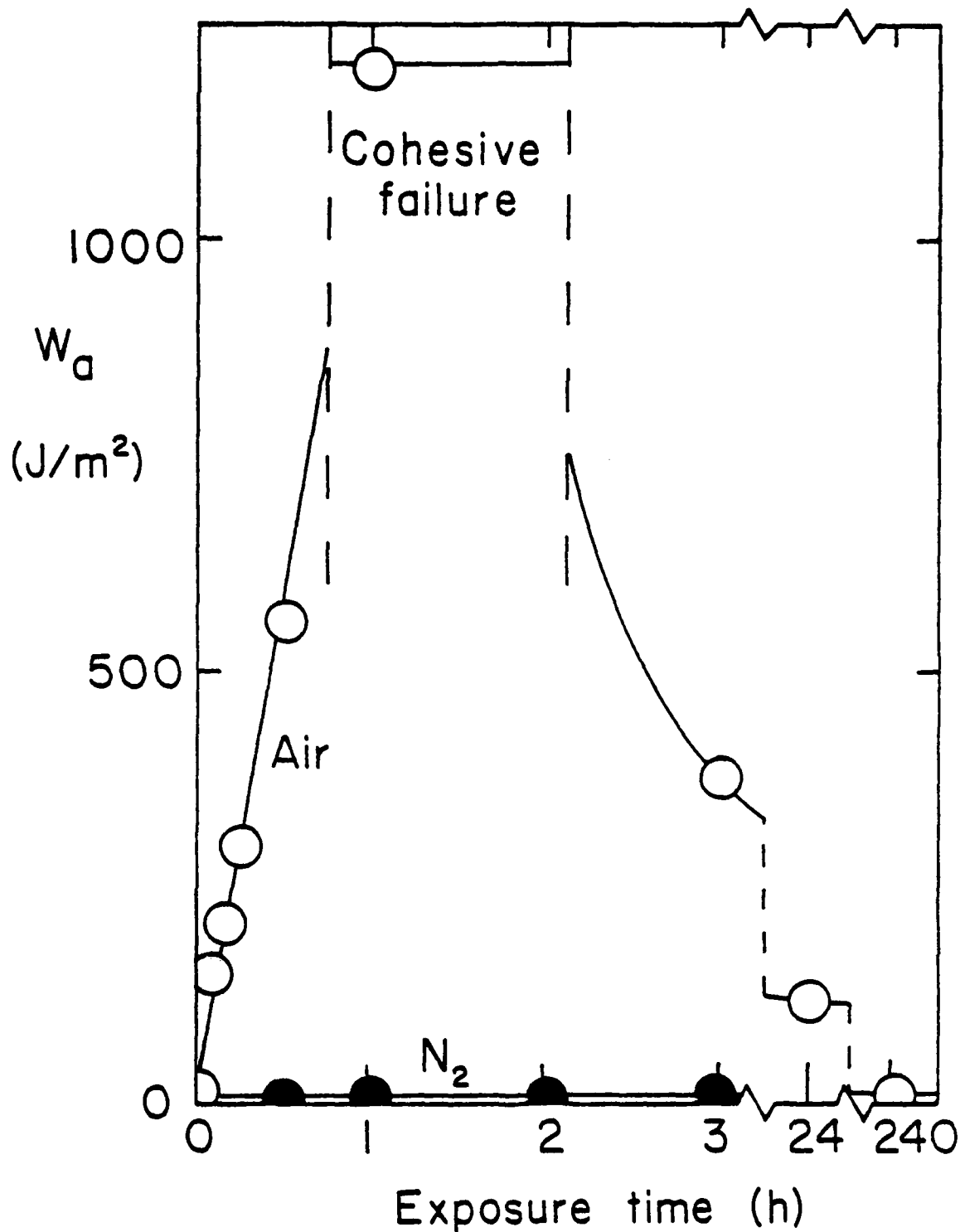


Figure 1. Work  $W_a$  of separation vs time of exposure to air or to nitrogen before bringing strips of Diene 35 NFA into contact. Peroxide recipe (0.05 per cent dicumyl peroxide).

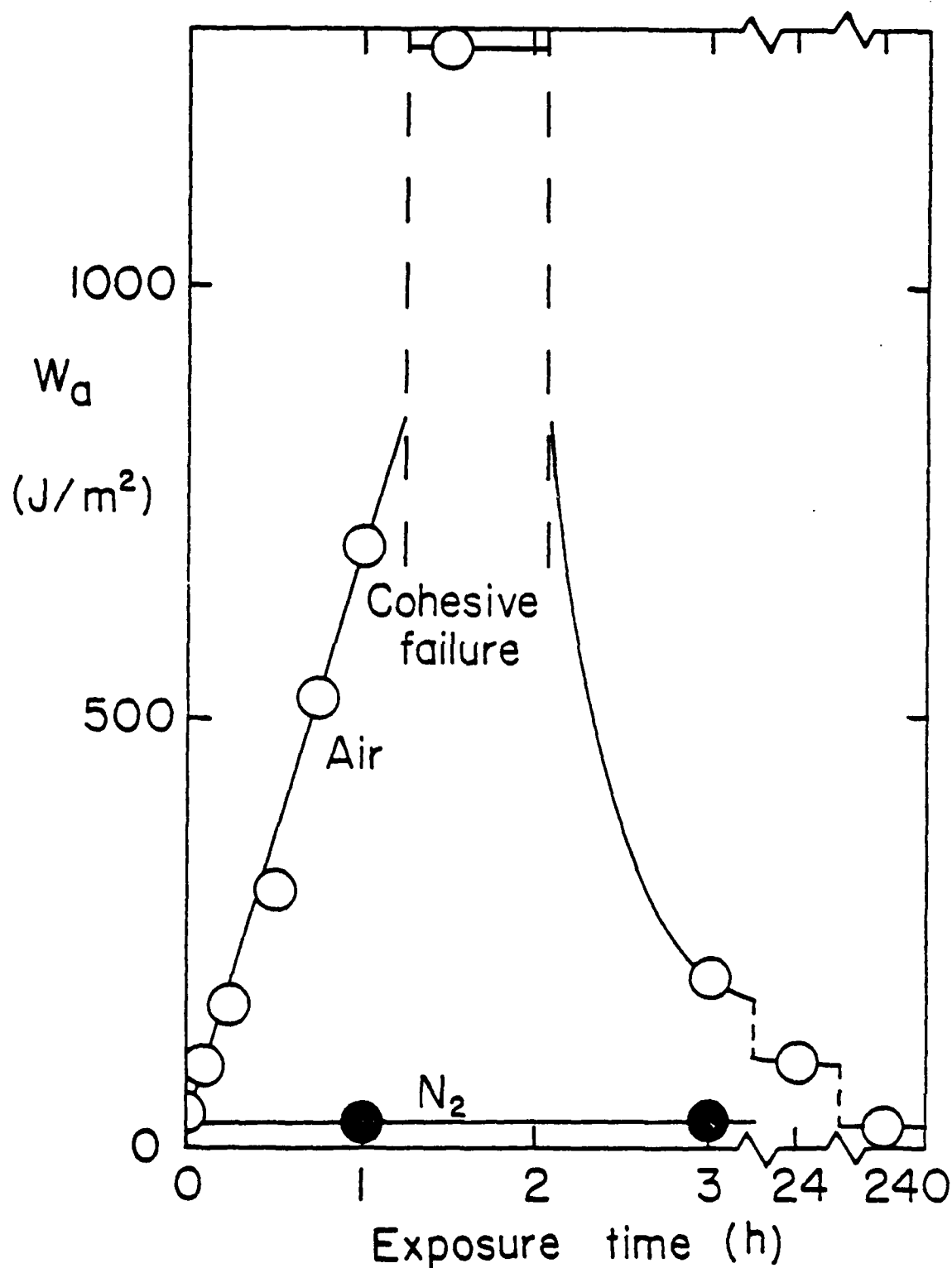


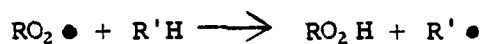
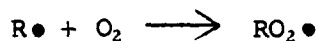
Figure 2. Work  $W_a$  of separation vs time of exposure to air or to nitrogen before bringing strips of Cis-4 polybutadiene into contact. Peroxide recipe (0.1 per cent dicumyl peroxide).

manufacturer may have been changed over a period of years. Even after extraction with hot acetone, however, the samples did not develop self-adhesion as rapidly, or to the same degree, as earlier samples. Either the added antioxidants are difficult to remove by this method or the new material is itself more resistant to oxidation. This aspect of oxidative interlinking is being examined further.

In striking contrast to the strong self-adhesion developed in polybutadiene materials, no comparable effect was observed with natural or synthetic cis-polyisoprene. Indeed, the self-adhesion of crosslinked layers of natural rubber was found to be decreased somewhat by prior exposure to air.

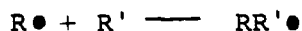
Now, it is well-known that oxidative reactions lead to further crosslinking and hardening of polybutadiene vulcanizates whereas, in contrast, they generally lead to softening of polyisoprene vulcanizates as a result of molecular scission (1-4). Contact angle measurements were consistent with oxidative reactions occurring in the surface regions of all the elastomers studied. However, the reaction resulted in strong adhesion only for the polybutadiene materials. This suggests that interfacial bonding is due to a particular feature of the oxidation of the polybutadiene that is not shown by polyisoprene. One particular mechanism is outlined below.

Oxidation of polyolefins is reported to involve two main propagation steps (1-4).



In the first, a polymer radical reacts with oxygen to form the peroxy radical which, in the second step, abstracts H from a nearby group to form a hydroperoxide and a second radical. Moreover, the hydroperoxide itself decomposes slowly, generating further radical species, so that the process is autocatalytic.

This general reaction scheme does not account for hardening during oxidation. Another reaction must therefore be invoked: the addition of polymer radicals to other polymer molecules to form intermolecular bonds.



This reaction is known to occur in polybutadiene by addition to the C-C double bond but not to a significant degree in polyisoprene where the radicals appear to be less reactive. It can thus account for the interfacial bonding observed with polybutadiene but not with polyisoprene. Moreover, it will become of proportionately greater importance as the concentration of oxygen becomes lower, i.e., as oxidation continues in the interfacial region after the elastomer layers have been brought into

contact. We therefore infer that the observed adhesion is due to the attack of polymer free radicals, generated during oxidation, upon molecules lying on the other side of the interface, to bring about covalent interlinking.

## 2. Effect of Number of Chemical Bonds

Studies of the effect of chemical bonding on the joint strength of adhesive bonds formed between polybutadiene and glass were carried out. The number of chemical bonds was determined using  $^{14}\text{C}$  labelled interfacial bonds and measuring the resulting radioactivity. The method of synthesis was described in Annual Report 3. Joint strength was measured using the  $180^\circ$  peel test with the slightly modified specimen shown in Figure 3. Measurements of the peel force were carried out sequentially on the two sides of the slides using the same procedure previously described by Runge and Dreyfuss (5). Work of adhesion,  $W$ , per unit area of interface was calculated from the time average peel force,  $P$ , per unit width,  $w$ , of the detaching layer:  $W = 2P/w$ . All tests were carried out at 0.5 cm/min crosshead speed.

The results of the study are plotted in Figure 4 where the observed work of adhesion is plotted against both  $\beta$ -emission and the number of glycine molecules per  $100 \text{ \AA}^2$ . The number of glycines is equal to the number of interfacial bonds. The

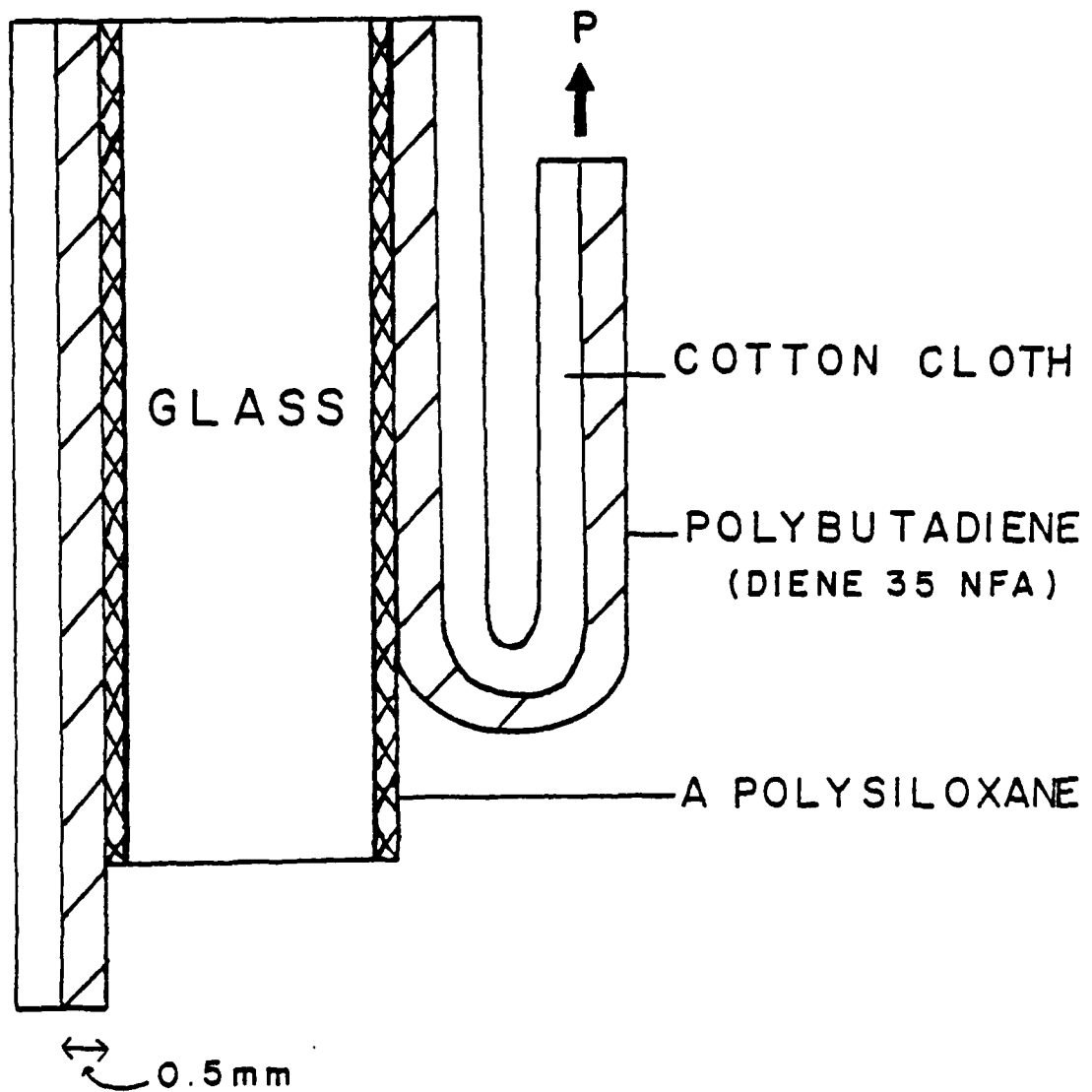


Figure 3. Diagram of Peel Test Specimen

data are based on what appears to the eye to be interfacial failure at the glass-rubber interface. Several conclusions can be drawn from the results shown in the Figure:

1. As the number of glycine/100  $\text{\AA}^2$  increases, the work of adhesion increases.
2. There are relatively few instances in which the number of glycine/100  $\text{\AA}^2$  is greater than 4. By far the largest number of points lie between two and four glycine/100  $\text{\AA}^2$ , although the mole fraction of 1-trichlorosilyl-2-(p,m-chloromethylphenyl)-ethane in the treating solution was varied from 0 to 1. The number of such silane molecules in the interphase determines the maximum number of radioactive glycine molecules that can be present. This measured number of chemical bonds is of about the same order of magnitude as the number of OH groups/100  $\text{\AA}^2$  usually quoted for glass dried under our conditions (6-8). This suggests a near 1:1 correlation between the number of interfacial bonds and the number of OH groups on the glass surface and indicates that the polysiloxane layer is probably no more than 1-2 layers thick.

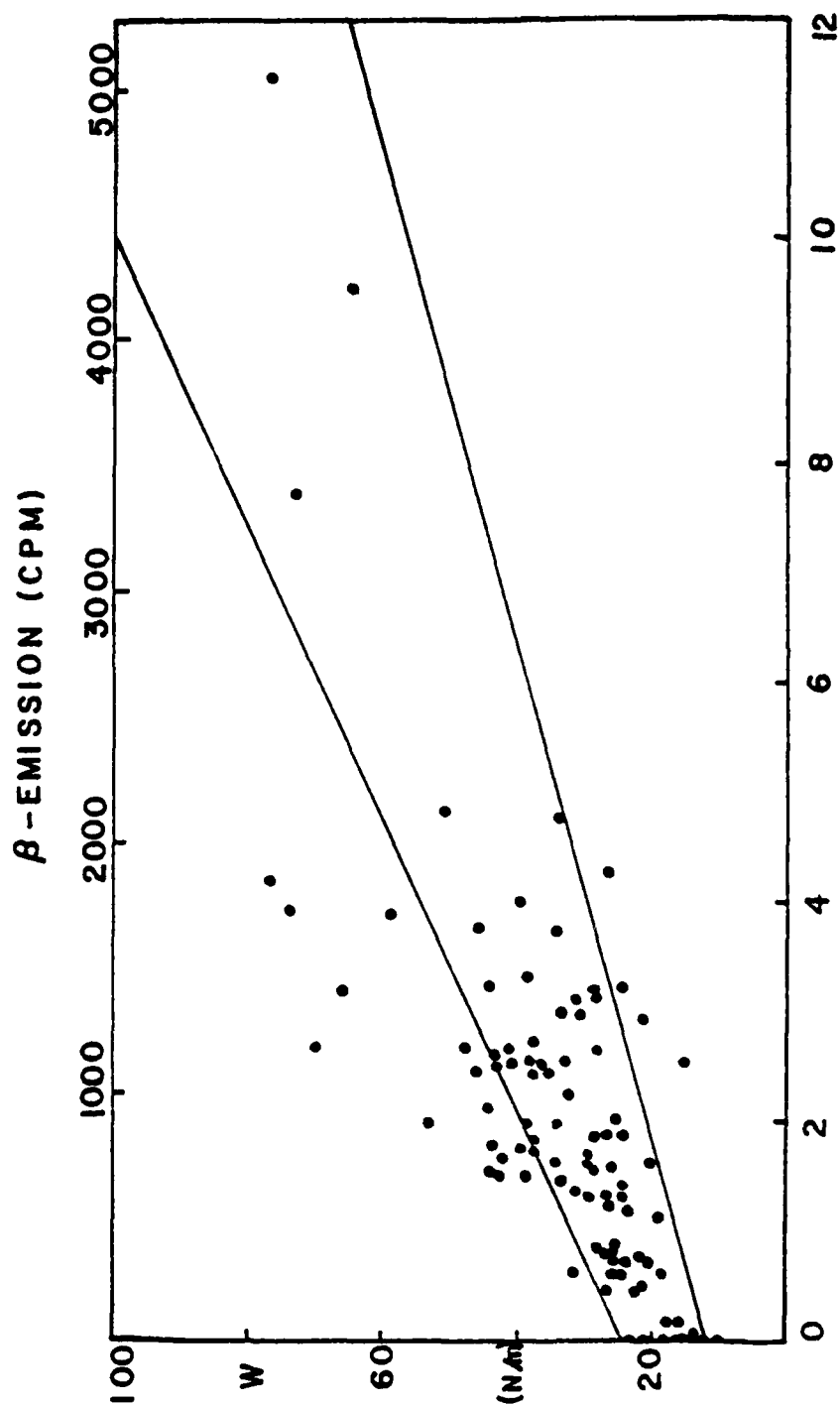


Figure 4. Effect of Number of Chemical Bonds on the Observed Work of Adhesion between Silanated Glass Surfaces and a Polybutadiene Adhesive



3. As the number of glycine/100 Å<sup>2</sup> increases, the scatter in the data also increases. We believe the scatter is real and results from an increasing amount of tearing through the polybutadiene toward the cloth. At higher peel forces patches of rubber on the glass were always visible to the eye. Therefore, instead of making a statistical analysis which would give one line and a coefficient of correlation, we have elected to draw two lines that encompass most of the data and give slightly greater weight to the lower values.
4. The slope of the lines is a measure of the increase in the work per interfacial chemical bond. This slope lies between 5 and 8 x 10<sup>-18</sup> J/bond and is of the same order of magnitude as C-N, C-C, and C=C bond strengths found in the literature (9). Table 1 shows the numerical comparisons. The experimental value is only one order magnitude higher than the bond strengths. The comparison would be even better if dispersion and van der Waals forces are considered (10). Furthermore, experimentally at any given time it is not possible to stress only one bond of a crosslinked network. Some work must be expended stretching several bonds

Table I

Comparison of Typical Bond Strengths With Observed Increase  
in Work of Adhesion per Chemical Bond

<u>Bond</u>	<u>E: J/Bond<sup>a</sup></u>	<u>Slope/E<sup>b</sup></u>
C-N	$0.5 \times 10^{-18}$	9-15
C-C	$0.6 \times 10^{-18}$	8-13
C=C	$1.2 \times 10^{-18}$	4-6

<sup>a</sup>Values in reference 14 are at 298°K.

<sup>b</sup>The experimental slope is  $(4.8-7.7) \times 10^{-18}$  J/glycine

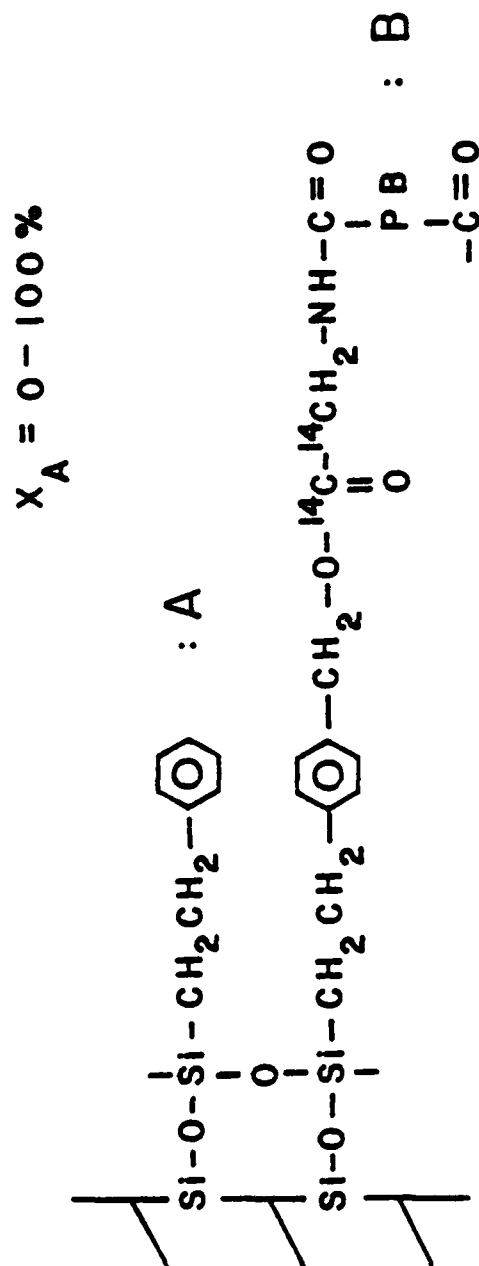
simultaneously and this would lead to observed forces being higher than theoretical forces. Thus we feel that there is reasonable agreement between the slope and bond strengths.

Bonds between silicon and oxygen or between silicon and carbon were not included in Table 1 because after peeling, essentially all the radioactivity remained on the glass surface. Considering that the interface has the structure shown in Figure 5, this indicates that fracture must have occurred within the polybutadiene or at one of the C-N bonds.

Since a correlation exists between the number of interfacial bonds of the model adhesive described in this report and the resulting joint strength, we conclude that chemical bonds at the interface improve adhesion of a properly prepared joint.

### 3. Studies of Model Filled Elastomer

Simple elastomers filled with glass beads or other model fillers have been shown to be stiffer, and sometimes stronger, than the corresponding unfilled material (11-14). Large changes have been associated with "dewetting", when the elastomer detaches from the glass beads at high strains to form vacuoles. When dewetting is pronounced, then the presence of the glass beads is stated to have no effect on the tensile properties (15).



**Figure 5. Structure of the Interface to which Polybutadiene Adhesive is Bonded**

In order to study the process of fracture in glass-filled elastomers in more detail, it thus seems advisable to control the tendency of the elastomer to dewet from the glass. Glass microspheres have therefore been obtained with a variety of surface pretreatments. In some instances; for example, when the glass had been treated with vinyltriethoxysilane; chemical bonding to the elastomeric matrix would be expected to occur during the free-radical crosslinking of the diene elastomer itself after the glass filler had been incorporated. In other instances; for example, when the glass had been pretreated with dimethyldiethoxysilane or had received no pretreatment at all; then no interfacial chemical bonding between the elastomeric matrix and the glass filler particles would be expected to occur when the elastomer was later crosslinked.

Model filled compounds were prepared using these treated and untreated glass microspheres, by mixing 50 phr into 100 phr polybutadiene, together with 0.05% of a free-radical crosslinking agent, dicumyl peroxide. These mixes were then pressed into sheets and the elastomeric matrix was crosslinked by heating at 150°C for 2 hrs. Tensile fracture experiments and measurements of tear strength, hysteresis and swelling ratio

were carried out on the resulting materials.

### Tensile Properties

The results of the tensile fracture experiments are given in Table 2. Data for unfilled rubber is included for comparison. The nominal breaking stress was higher and the elongation at break was lower for the compound filled with glass beads pretreated with vinyltriethoxysilane, which is expected to form chemical bonds with the elastomer, and for the glass beads pretreated with n-propylaminotriethoxysilane. Indeed, the values obtained are higher than for unfilled elastomer and the specimens showed stress whitening before rupture. Compounds filled with glass treated with non-bonding silanes, dimethyldiethoxysilane and octadecyltriethoxysilane, had lower breaking stresses and lower breaking elongations than unfilled material. These specimens also showed substantial stress whitening before rupture. Nominal breaking stress of compounds containing untreated glass was higher or lower than unfilled material, depending on the size of filler added but the elongation at break was always lower than for unfilled elastomer.

An alternative measure of the strength in tension is given by the strain energy density at break,  $U_b$ . These values are given in the final column of Table 2. The results show a

Table 2

Tensile properties of glass-filled polybutadiene. Volume fraction of glass = 0.16

Diameter of glass particles $\mu\text{m}$	Glass treatment <sup>a</sup>	Nominal breaking stress, $\bar{\sigma}_b$ (MPa) <sup>b</sup>	Breaking elongation, $e_b$ <sup>b</sup>	Strain energy density at break, $U_b$ (MJ/m <sup>3</sup> ) <sup>c</sup>
No glass	-	0.85 $\pm$ 0.03	2.06 $\pm$ 0.18	0.88
<u>Effect of coating</u>				
80-220	AS	1.00 $\pm$ 0.025	1.23 $\pm$ 0.15	0.62
80-220	VS	0.88 $\pm$ 0.01	1.18 $\pm$ 0.05	0.52
80-220	none	0.87 $\pm$ 0.015	1.38 $\pm$ 0.10	0.60
80-220	DMS	0.80 $\pm$ 0.01	0.95 $\pm$ 0.08	0.38
80-220	OS	0.57 $\pm$ 0.008	1.34 $\pm$ 0.10	0.38
<u>Effect of size</u>				
30-95	none	0.81 $\pm$ 0.04	1.73 $\pm$ 0.04	0.70
80-220	none	0.87 $\pm$ 0.015	1.38 $\pm$ 0.10	0.60

<sup>a</sup>AS: n-propylaminotriethoxysilane  
 VS: vinyltriethoxysilane  
 DMS: dimethyldiethoxysilane  
 OS: octadecyltriethoxysilane

<sup>b</sup>Crosshead speed = 8mm/s. Rate of elongation  $\approx 0.2\text{s}^{-1}$ . Eight separate measurements were made on each sample.  $e_b = \Delta L/L_0$  where  $\Delta L$  is the increase in length from an initial length  $L_0$  to a final length at break  $L_b$ .

<sup>c</sup> $U_b = (\bar{\sigma} e_b)/2$  assuming linear stress-strain relationships were followed up to break. Since the observed stress-strain curves become markedly concave to the strain axis near rupture, this procedure somewhat underestimates the true value of work expended in breaking the specimen.

marked decrease in  $U_b$  on adding glass filler, even when the glass was pretreated with a bondable silane, and a further large decrease when the glass was pretreated with a non-bonding silane.

#### Tear Strength

Measurements of fracture energy, or tear strength,  $T$  were carried out on 5 or more strips of each compound. The values obtained were found to vary by about  $\pm 15$  per cent, even though the tear force had been preaveraged along the length of each strip. The mean values of tear strength are given in Table 3. They are seen to be significantly increased by adding glass particles, by about 25 per cent for the larger sized particles. Moreover, the tear strength does not appear to depend upon the degree of interfacial bonding to a significant degree. The tear strength is somewhat higher for the compound containing non-bonding octadecyltriethoxysilane coated glass particles; but this may reflect merely the enhanced energy dissipation of this material on deformation. The low value of tear strength for the compound containing glass particles coated with dimethyldiethoxysilane may result not only from non-bonding to the elastomer but also from poorer bonding to



Table 3

Tear strength of glass-filled polybutadiene. Volume fraction of glass = 0.16

Diameter of glass particles, $\mu\text{m}$	Glass treatment <sup>a</sup>	Tear strength, $T(\text{J/m}^2)$ <sup>b</sup>	Depth of crack, $c(\mu\text{m})$ <sup>c</sup>
No glass	-	405	110
<u>Effect of coating</u>			
80-220	AS	530	220
80-220	VS	490	240
80-220	none	520	220
80-220	DMS	400	260
80-220	OS	560	370
<u>Effect of size</u>			
30-95	none	440	160
80-220	none	520	220

<sup>a</sup>See Table 2 for the meaning of the symbols.<sup>b</sup>Measured at 0.5 cm/min crosshead speed  $\approx$  a rate of tear of 40  $\mu\text{m/s}$ .<sup>c</sup>Calculated assuming that the elastic strain energy density at break,  $U_b$ , is given by  $U_b = T/2 \text{ kc(11)}$  where  $T$  is the fracture energy (tear strength),  $k$  is a numerical quantity which may be assigned the value 2 for moderate deformations and  $c$  is the depth of an edge nick, i.e.  $c = T/4U_b$ .

the glass of a weaker polysiloxane network from the diethoxysilane. All other polysiloxane coatings were obtained from triethoxysilanes.

It seems likely that the intrinsic tear strength of the filled materials is not much different from that of the elastomeric matrix. The main effect of the filler particles is apparently to cause a deviation of the tear path from a straight line, so that the tear becomes rougher. A noticeable increase in roughness of the torn surface was observed in comparison with that of the unfilled material. The scale of roughness is probably set by the size of the filler particles; it is noteworthy that the larger glass particles gave higher tear strength compounds. However, if the particle size is smaller than the natural tear roughness of the unfilled elastomer, then they would presumably have little influence on the tear strength by this particular mechanism of enforced deviation of the tear path.

#### Fracture nuclei in tension

The depth,  $c$ , of a nick or flaw from which tensile fracture initiates may be calculated from the measured tear energy  $T$  and the fracture energy density,  $U_b$ . Values obtained in this way are given in the last column of Table 3. They are

seen to be significantly larger for the glass-filled materials than for the unfilled elastomer, and to be generally of the same order of magnitude as the diameter of the largest glass particles present. The only significant exception is shown by the last material, for which the filler bonding is least strong and dewetting is most pronounced. In this case, the initial fracture nucleus may be a larger flaw associated with several contiguous dewetted particles.

Nevertheless, the general correlation shown in Table 3 between the calculated flaw size and the size of the glass particles, for materials having a wide range of values of  $\underline{U_b}$ , strongly suggests that tensile rupture in elastomers containing solid particles takes place by catastrophic tearing from an initial flaw which may be identified with an unusually large dewetted particle. Clearly, when the particle size is smaller than the size of adventitious flaws, about 50  $\mu\text{m}$  in the present case, then this correlation will cease to hold. Work with other sizes of glass beads, both larger and smaller than the ones used in this study, is in progress.

#### Hysteresis

Energy dissipation was clearly greater for filled than for unfilled materials. This is seen in the results of measurements

of mechanical hysteresis shown in Table 4. The differences in hysteresis of coated and uncoated glass beads are small except for the higher values obtained from materials containing glass beads treated with octadecyltriethoxysilane. This probably results from greater dewetting with these beads.

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Helpful suggestions and advice were received from J. N. Henderson of the Goodyear Tire and Rubber Co. The authors thank K. Riew of the BFGoodrich Co. for supplying a sample of carboxyterminated polybutadiene, Hercules, Inc. for supplying the Dicap-R, and the Firestone Tire and Rubber Co. for samples of Diene 35 NFA.

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A. N. Gent, Professor (6%)  
P. Dreyfuss, Research Associate (50%)  
K. Sehgal, Postdoctoral Research Fellow (100% for 3 months)  
Y. Eckstein, Postdoctoral Research Fellow (100%) for 5 months)  
J. A. Hartwell, Graduate Research Student (100% for 3 months)  
R. H. Tobias, Graduate Research Student (100% for 3 months)  
S. Tremelin, Graduate Research Student (100% for 3 months)  
J. R. Williams, Student Assistant (100% for 3 months)

Table 4

Mechanical hysteresis,  $H$ , on stretching to specified elongation and retracting<sup>a</sup>

Diameter of glass particles, $\mu$ m	Glass treatment <sup>b</sup>	Elongation before retraction, e <sup>c</sup>			
		0.25	0.5	0.75	1.0
No glass	-	0.12	0.009	0.009	0.009
<u>Effect of coating</u>					
80-220	AS	0.12	0.12	-	-
80-220	VS	0.16	0.16	-	-
80-220	none	0.16	0.14	0.14	-
80-220	DMS	0.12	0.17	-	-
80-220	OS	0.22	0.22	0.17	-
<u>Effect of size</u>					
30-95	none	0.16	0.20	0.17	0.17
80-220	none	0.16	0.14	0.14	-

<sup>a</sup>The hysteresis ratio,  $H$ , defined as the energy dissipated relative to the energy supplied in stretching the specimen, was determined from the areas  $A_1$  and  $A_2$  under the loading and unloading force-displacement relations when specimens were stretched at a rate of elongation of about  $0.01\text{s}^{-1}$  (2 cm/min crosshead speed) and then allowed to retract at the same rate back to the unstrained state.  $H = (A_1 - A_2)/A_1$ . The same sample was stressed repeatedly.

<sup>b</sup>See Table 2 for the meaning of the symbols.

<sup>c</sup> $e = \Delta L/L_0$  where  $\Delta L$  is the increase in length from an initial length  $L_0$  to a final length  $L$ .

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